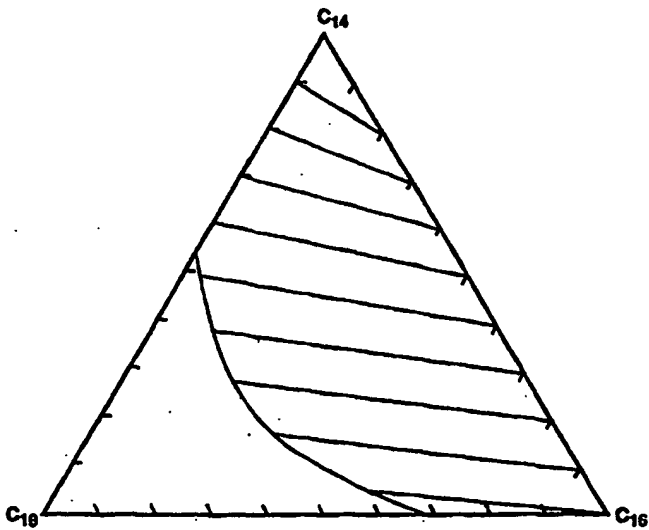


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(21) International Application Number: PCT/US95/01263 (22) International Filing Date: 31 January 1995 (31.01.95) (30) Priority Data: 08/190,405 2 February 1994 (02.02.94) US (71) Applicant: CHEVRON CHEMICAL COMPANY [US/US]; P.O. Box 7141, San Francisco, CA 94120-7141 (US). (72) Inventors: GEE, Jeffrey, C.; 3810 Birch Villa, Kingwood, TX 77345 (US). LAWRIE, Christophe, J.; 2022 Red Magnolia Court, Kingwood, TX 77339 (US). WILLIAMSON, Roger, C.; 1420 Sycamore Lane, Kingwood, TX 77339 (US). (74) Agents: PRIESTER, Witta et al.; Chevron Corporation, Law Dept., P.O. Box 7141, San Francisco, CA 94120-7141 (US).		(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ). Published <i>With international search report.</i>
(54) Title: DRILLING FLUIDS COMPRISING MOSTLY LINEAR OLEFINS		
		
(57) Abstract <p>The invention relates to fluids used in subterranean oil and gas wells, especially drilling fluids comprising mostly linear olefins, preferably C₁₄ to C₁₈ olefins. It also relates to invert emulsion drilling fluids where the continuous phase is a synthetic hydrocarbon comprising mostly linear olefins.</p>		

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01 DRILLING FLUIDS COMPRISING MOSTLY LINEAR OLEFINS

02

03 BACKGROUND OF THE INVENTION

04

05 This invention relates to drilling fluids used in the
06 drilling of subterranean oil and gas wells as well as
07 other drilling fluid applications and drilling
08 procedures. The invention is particularly concerned with
09 synthetic hydrocarbons, and especially hydrocarbon
10 mixtures containing mostly linear olefins, preferably
11 with carbon numbers between 14 and 18. These synthetic
12 hydrocarbons exhibit minimal toxicity toward aquatic life
13 and possess desirable rheological and filtration control
14 properties for use in drilling fluids.

15

16 The use of synthetic hydrocarbons, particularly
17 oligomerized olefins, for drilling fluids has recently
18 been patented. For example, Mercer et al. in U.S. Patent
19 No. 5,096,883 disclose the use of compositions consisting
20 essentially of branched paraffins having between 16 and
21 40 atoms per molecule (such as the hydrogenated dimer of
22 1-decene) for this use. Also, Patel et al. in U.S.
23 Patent No. 5,189,012 disclose the use of compositions
24 comprising branched chain oligomers having an average
25 molecular weight of from 120 to 1000 in drilling fluids.
26 These synthetic hydrocarbons are prepared by
27 oligomerizing one or more olefinic monomers having a
28 chain length of C₂ to C₁₄. The full disclosure of these
29 two references is incorporated herein by reference.

30

31 One well-known method for oligomerizing olefins utilizes
32 a boron trifluoride catalyst. However, boron trifluoride
33 is toxic and, upon contact with water or steam, produces
34 toxic and corrosive fumes. Moreover, disposal of boron
35 trifluoride residues presents an environmental problem.
Therefore, a novel process to produce synthetic
hydrocarbons useful for drilling fluids from non-

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01 hazardous reagents utilizing a non-hazardous, non-
02 polluting catalyst would be a significant improvement in
03 the art.

04
05 Additionally, only a small fraction of the commercially
06 available products of olefin oligomerization are useful
07 in drilling fluids. Thus, the synthetic hydrocarbons
08 used in the above-mentioned patents are often in short
09 supply and so are not always readily available.

10
11 The long-felt need described in these patents for an
12 environmentally acceptable, fully functional, and readily
13 available synthetic hydrocarbon for use in synthetic
14 hydrocarbon-based drilling fluids has not yet been
15 satisfied; that is, not until the invention described
16 hereinbelow.

17

18 SUMMARY OF THE INVENTION

19

20 In one embodiment, the present invention is a continuous
21 phase for a synthetic hydrocarbon-based drilling fluid
22 comprising mostly linear olefins, where the olefins have
23 at least 12 carbon atoms. An especially preferred
24 composition has olefins containing between 14 and 18
25 carbon atoms.

26

27 In another embodiment, the present invention is an invert
28 emulsion drilling fluid which includes a mixture of
29 mostly linear olefins as the continuous phase, a weight
30 material, and water. Optionally, the drilling fluid can
31 contain emulsifiers, viscosifiers, fluid-loss additives,
32 and other specific additives designed to impart desirable
33 properties to the fluid.

34

35 Among other factors, the present invention is based on
the unexpected discovery that, although normal alpha-
olefins (NAO) are not generally useful in synthetic

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01 hydrocarbon-based drilling fluids, mixtures of mostly
02 linear olefins are minimally toxic and highly effective
03 as the continuous phase of drilling fluids.

04

05 BRIEF DESCRIPTION OF THE DRAWING

06

07 The figure is a ternary diagram showing compositional
08 mixtures, in terms of weight percent, for C₁₄ NAO and
09 isomerized normal alpha-olefins having sixteen and
10 eighteen carbon atoms. The shaded area shows
11 compositions of this invention.

12

13 DETAILED DESCRIPTION OF THE INVENTION

14

15 A mixture of "mostly linear" olefins, according to the
16 present invention, is a mixture of olefins in which the
17 majority of olefins are linear olefins, i.e., non-
18 branched olefins. Such mixtures may even, but not
19 necessarily, consist wholly of linear olefins. Linear or
20 normal olefins for the purposes of this invention are
21 straight chain, non-branched hydrocarbons with at least
22 one double carbon-carbon bond present in the chain.

23

24 Preferred mixtures are those comprising mostly linear
25 olefins with 12 or more carbons. Preferably, the linear
26 olefin will contain between 12 and 24 carbon atoms, more
27 preferably between 14 and 18 carbon atoms. Both odd and
28 even number olefins can be used. One useful composition
29 is prepared by double-bond isomerization of one or more
30 NAO's having between 14 and 18 carbon atoms. In the
31 mixtures of this invention, the majority of olefins are
32 linear i.e., the mixtures are "mostly linear" or
33 predominately linear. The term mostly linear as used
34 herein means that between 50 and 100%, preferably between
35 60 and 100%, and more preferably between 70 and 80% of
the olefins in the mixture do not have branch points
along the hydrocarbon chain. On the other hand, it is

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01 further preferred that such mixtures also contain olefins
02 with some side-chain branching. It is preferred that the
03 branched olefins comprise at least 5%, preferably at
04 least 10% of the mixture. Preferably, these mixtures are
05 substantially free of aromatics. The special benefits of
06 such mixtures will be described below.

07

08 Commercially available linear olefins, such as normal
09 alpha olefins with 14 to 18 carbon atoms or more, have
10 many of the desired properties of synthetic hydrocarbons
11 useful as the continuous phase of a synthetic
12 hydrocarbon-based drilling fluid including kinematic
13 viscosity, flash point, and sheen properties.
14 Unfortunately, the pour points of such materials are
15 typically too high. However, we have found that mixtures
16 of mostly linear olefins containing substantial amounts
17 of internal olefins and small amounts of branched
18 olefins, are useful in drilling fluids. Such mixtures
19 can include, but are not limited to, mixtures containing
20 C₁₄, C₁₆, or C₁₈ normal alpha- and linear internal
21 olefins, or combinations thereof.

22

23 There are several ways to make compositions of this
24 invention. For example, the mixture of olefins can be
25 made by blending a number of commercially available
26 olefins (i.e., linear alpha, linear internal, branched
27 alpha and branched internal). For example a mixture of
28 C₁₄ to C₁₈ linear internal olefins can be blended.

29

30 The linear olefins useful in this invention can be made
31 in various ways, which are well known to those skilled in
32 the art. These methods include, but are not limited to:
33 cracking of linear paraffins; metathesis or
34 disproportionation of olefins, especially alpha-olefins;
35 oligomerization of ethylene; dehydrogenation of linear
paraffins; and double bond isomerization of normal alpha-
olefins.

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01 One preferred preparation method involves catalytic
02 olefin isomerization with or without skeletal
03 isomerization. For instance, a platinum supported on a
04 SAPO-11 molecular sieve catalyst can be used to partially
05 isomerize a feed containing C₁₄ to C₁₈ olefins. This and
06 related catalysts are described in U.S. Patent No.
07 5,082,986. Other useful catalysts are well known in the
08 art.

09
10 For platinum on SAPO-11 catalysts, partial isomerization
11 is preferred. Therefore, preferred operating conditions
12 include weight hourly space velocities (WHSV's) between
13 0.5 and 10 at temperatures between 120° and 220°C. More
14 preferred conditions include WHSV's of between 0.5-5 at
15 temperatures of 120-160°C; most preferred conditions
16 include WHSV's of between 0.5-3.5 at temperatures of
17 about 120-140°C. Lower temperatures result in
18 substantial olefin double bond migration, while higher
19 temperatures result in increased skeletal rearrangement.
20 The process is preferably conducted in the absence of
21 added hydrogen.

22
23 The feed is preferably a mixture of linear olefins,
24 preferably containing or consisting essentially of normal
25 alpha-olefins. The feed can contain components of only
26 one carbon number, or it can contain components of two or
27 more different carbon numbers. Generally, each component
28 has at least 12 carbon atoms; preferably between 12 and
29 24 carbon atoms, most preferably between 14 and 18 carbon
30 atoms.

31
32 One preferred product is a mixture of linear and branched
33 olefins; it may comprise products derived from a single
34 olefin, or it may comprise a blend of products derived
35 from a number of different olefins. The resulting
mixture of mostly linear olefins is predominately
internal olefins, typically having less than 20% alpha-

-6-

01 olefin. About 10 to 45% of the product is branched
02 rather than linear; typically the product is 20 to 40%
03 branched.

04

05 Although discussed herein in terms of olefinic products,
06 the product hydrocarbons of this invention can be
07 hydrogenated to achieve complete or preferably partial
08 saturation. These hydrogenated products are also
09 intended to be encompassed by the term "olefins" as used
10 herein. However, the unhydrogenated hydrocarbons are
11 preferred.

12

13 The present inventors have demonstrated that drilling
14 fluid formulations containing mixtures comprising mostly
15 C₁₄ normal alpha-olefins are functional. However, the
16 amount of C₁₃ and lower normal alpha-olefins that can be
17 used is limited by undesirable flash point properties and
18 the amount of C₁₅ and higher normal alpha-olefins limited
19 by undesirable pour point properties. Depending on the
20 composition of the various components, in some cases C₁₄
21 NAO can be blended with isomerized C₁₆ and/or isomerized
22 C₁₈ product to produce mixtures having useful properties
23 for drilling fluids.

24

25 The pour points of linear internal olefins are lower than
26 those of the corresponding normal alpha-olefins. And, we
27 have found that the former are especially useful in
28 drilling fluids.

29

30 The present inventors have determined that mixtures
31 comprising mostly linear internal olefins and
32 additionally containing single branched olefins are
33 particularly advantageous, in part because of the low
34 pour points of such mixtures. A preferred product of the
35 current invention has a pour point of less than -5°C and
will remain liquid and homogeneous after standing at -5°C

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01 for at least one week. The viscosity of the product
02 mixture at 100°C will preferably be 1.3-1.7 cSt.

03

04 Based on the description above, a phase diagram showing
05 acceptable products for the continuous phase of a
06 drilling fluid can be constructed. The figure is an
07 example of one such diagram. It shows regions of
08 acceptable (shaded) and unacceptable blends of 1-
09 tetradecene with C₁₆/C₁₈ mixtures. This figure was
10 developed using a C₁₆/C₁₈ mixture having about 22%
11 branched products (primarily methyl branched), about 10%
12 normal alpha-olefin and about 68% linear internal
13 olefins. The C₁₆/C₁₈ components for this figure were
14 prepared by individually isomerizing a C₁₆ and a C₁₈ NAO
15 at 180°C at a WHSV of 1.6. For this figure, acceptable
16 blends were defined as those that remained essentially
17 clear and homogeneous after standing for two days at -
18 10°C.

19

20 Mostly Linear Olefins in Drilling Fluids

21

22 One embodiment of the present invention is the use of
23 mixtures of mostly linear olefins as the synthetic
24 hydrocarbon in the continuous phase of invert, or
25 water-in-oil, emulsion type drilling fluids. In another
26 embodiment, this invention is a synthetic hydrocarbon-
27 based drilling fluid containing primarily, i.e. greater
28 than 80% and preferably greater than 90%, linear olefins.

29

30 Synthetic hydrocarbons used in downhole drilling fluids,
31 especially offshore, must have at least five properties.
32 These are low pour point, low viscosity, acceptable flash
33 point, lack of sheen, and minimal toxicity. Preferred
34 products of this invention have all these properties.

35

More particularly, the synthetic hydrocarbons preferably
have a pour point below about 0°C. In offshore drilling,

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01 the drilling fluid may see the ambient ocean temperature
02 in the riser, the section of pipe between the seabed and
03 the drilling platform that is exposed to the ocean. Such
04 temperatures can be close to 0°C in the North Sea, for
05 example, and the use of a synthetic hydrocarbon with a
06 pour point higher than 0°C may result in an unacceptable
07 rise in the drilling fluid's viscosity, or even in severe
08 thickening of the drilling fluid. Such phenomena can
09 result in the drilling fluid's dispersing in the
10 underground rock strata. More preferably, the synthetic
11 hydrocarbon has a pour point below about -5°C and remains
12 homogenous after standing at -5°C for at least one week.
13 Most preferably the pour point is below about -9°C.

14

15 The derived kinematic viscosity of the drilling fluid is
16 an important parameter since if it is too low, the
17 drilling fluid will not perform its function of
18 suspending the cuttings and bringing them to the surface;
19 however, if it is too high, pumping of the drilling fluid
20 will not be facile. While the derived kinematic
21 viscosity of the drilling fluid can be controlled by
22 additives, the viscosity of the synthetic hydrocarbon is
23 a primary factor. For that reason, the kinematic
24 viscosity of the synthetic hydrocarbon should be,
25 broadly, in the range of 0.5 to 5 centistokes (cSt) at
26 100°C. More preferably, the kinematic viscosity at 100°C
27 is between 1 to 3 cSt, and, most preferably, is between
28 1.3 to 1.7 cSt.

29

30 A further requirement for the synthetic hydrocarbon is
31 that it has a relatively high flash point for safety
32 reasons. Preferably, the flash point should be above
33 90°C. A flash point above 110°C is more preferred.

34

35 An additional requirement for the synthetic hydrocarbon
is that it not produce a sheen when added to water.
Unlike diesel fuels and other oils previously used in

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01 drilling fluid, the synthetic hydrocarbons of this
02 invention produce no sheen and thus fulfill this
03 requirement.

04

05 Additionally, the synthetic hydrocarbons of this
06 invention are minimally toxic to marine and animal life.
07 As invert emulsion drilling fluids, they exhibit minimal
08 toxicity as determined by a mysid shrimp (Mysidopsis
09 bahia) bioassay specified by the United States
10 Environmental Protection Agency (EPA). As shown in the
11 examples herein below, drilling fluids prepared using the
12 synthetic hydrocarbons of this invention are
13 environmentally compatible.

14

15 The drilling fluid compositions of the present invention
16 can be modified according to the end use of the fluid
17 using suitable weight materials, emulsifiers, wetting
18 agents, viscosifiers, densifiers, fluid-loss additives,
19 and the like. The fluids can also be used as workover
20 fluids, packer fluids, coring fluids, completion fluids,
21 and in other well-servicing applications.

22

23 The drilling fluid comprises a mixture of mostly linear
24 olefins and optionally methyl-substituted olefins as the
25 synthetic hydrocarbon or nonaqueous continuous phase.
26 The synthetic hydrocarbon may comprise up to 100% by
27 volume of the drilling fluid composition. Preferably,
28 water is added as part of the composition and the aqueous
29 phase may comprise up to 70% by volume of the
30 composition.

31

32 Thus, the hydrocarbon preferably comprises at least 30%
33 by volume of the drilling fluid, more preferably between
34 about 50 to 70 volume percent. The aqueous phase may be
35 either fresh water or aqueous solutions containing salts
such as sodium chloride, potassium chloride, calcium
chloride, and combinations thereof. The salts function

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01 as a densifier and emulsion stabilizer, and also serve to
02 protect salt formations from dissolution in the drilling
03 fluid.

04

05 If the drilling fluid is formulated with a significant
06 water content, the aqueous phase is preferably dispersed
07 within the nonaqueous phase to form an invert emulsion.
08 In the absence of mechanical agitation, such emulsions
09 are generally unstable; so anionic surfactants are
10 commonly added. Hydrocarbon soluble anionic surfactants
11 are preferred for stabilizing invert emulsions. Useful
12 examples of such surfactants are the di- and trivalent
13 metal salts of fatty acids; other useful surfactants are
14 well known to those skilled in the art. The invert
15 emulsion can be further stabilized by adding
16 macromolecular surfactants. These include the polyamide
17 class of emulsifiers manufactured by the reaction of
18 polyamines with the combination of fatty acids and
19 dibasic acids such as maleic and fumaric acids.

20

21 The density of the drilling fluid of the present
22 invention can be adjusted by adding a weight material.
23 It is often desirable to increase the drilling fluid
24 density to prevent collapse of the formation into the
25 bore-hole. Weight materials are well known in the art and
26 include, but are not limited to: barium sulfate, calcium
27 carbonate, iron oxide, and the like. To avoid the weight
28 material settling out of high density drilling fluid
29 compositions, it is often desirable to add a wetting
30 agent. The emulsion stabilizing surfactants described
31 above will serve this function also; however, other
32 wetting agents can be added, if desired. These can
33 include polyethoxylated alkylphenols, polyethoxylated
34 alcohols, or polyethoxylated polyol fatty acid esters.

35

The suspending properties of the drilling fluid can be improved by adding a gellant or viscosifier. A commonly

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01 used viscosifier is an amine-treated clay. The clay will
02 also impart some desirable filtration control properties.
03 If further fluid loss control is desired, other additives
04 such as organophilic lignites, blown asphalt, uintaite or
05 other polymeric materials that will line the bore-hole
06 can be used.

07

08 Other hydrocarbons, such as those described in U.S.
09 Patent No. 5,096,883 and/or U.S. Patent No. 5,189,012,
10 may be blended with the synthetic hydrocarbons of this
11 invention provided that the final blend has the necessary
12 pour point, kinematic viscosity, flash point, and
13 toxicity properties to function as the continuous phase
14 of a synthetic hydrocarbon- based drilling fluid.
15 Additionally, the compositions may be modified by
16 including various additives, such as those discussed
17 above, to impart desirable properties to the drilling
18 fluid. However, the omission of other specific additives
19 in the discussion above is not intended to preclude their
20 use in the drilling fluid of this invention.

21

22 The mostly linear olefins of this invention can be
23 blended with other synthetic hydrocarbons, especially
24 olefins, either branched or linear and preferably
25 branched, in any proportion so long as the hydrocarbon
26 meets the performance characteristics of a drilling
27 fluid. An especially preferred blending agent is a
28 polyalpha-olefin (PAO), especially PAO's having between
29 16 and 24 carbon atoms.

30

31 Preferred drilling fluids of this invention have
32 performance properties equivalent to or better than
33 conventional oil-based drilling fluids. The synthetic
34 hydrocarbon of this invention can be used to prepare an
35 invert emulsion with excellent high temperature
stability. Indeed, the drilling fluid of this invention
exhibited better high temperature stability when compared

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01 to a drilling fluid prepared from a commercial 2 cSt
02 polyalpha-olefin synthetic hydrocarbon. Additionally,
03 functional suspending properties of the products are
04 indicated by the high yield points and acceptable gel
05 strengths. Moreover, the fluid loss properties are good,
06 even in the absence of a fluid loss additive.

07
08 Conventional oil-based drilling fluids exhibit
09 substantial toxicity to marine life and therefore the
10 cuttings from drilling operations with such fluids cannot
11 currently be disposed of offshore, necessitating costly
12 transport to shore and disposal in onshore hazardous
13 waste facilities. In contrast, the drilling fluid of
14 this invention exhibits minimal toxicity to marine life,
15 as evidenced by the excellent survival rates of mysid
16 shrimp exposed to the drilling fluid in bioassays
17 conducted according to the Protocol specified by the US
18 EPA.

19
20 Moreover, the derived viscosity of the fluid was also
21 lower, indicating that the drilling fluid of this
22 invention offers a faster drilling fluid. The present
23 inventors also contemplate that, alternatively, a
24 drilling fluid of similar derived viscosity to that
25 prepared using the commercial PAO could be prepared by
26 using a lower synthetic hydrocarbon to water ratio, thus
27 offering a more economical drilling fluid.
28 Furthermore, the synthetic hydrocarbons of the present
29 invention can be prepared in a variety of ways, such as
30 blending commercially available compounds or isomerizing
31 olefins as discussed above. Thus, these products offer
32 considerable flexibility in choice of feedstock.
33 Important properties of the synthetic hydrocarbon product
34 that affect the final properties of the drilling fluid,
35 such as kinematic viscosity and degree of branching, are
controllable in this invention to an extent unavailable
in practice to users of synthetic PAO's.

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01 Additionally, since synthetic PAO's are in short supply,
02 they are not always readily available. In part, this is
03 because only a small fraction of the product resulting
04 from oligomerization of, for example, 1-decene is useful
05 in drilling fluids. In contrast, the compositions of
06 this invention can be prepared from a variety of feeds.
07 These feeds, such as tetradecene, hexadecene, and
08 octadecene are commercially available products.

09

10

EXAMPLES

11

12 The invention will be further described by the following
13 examples. These examples are not intended to be
14 limiting, in any way, the invention being defined solely
15 by the appended claims.

16

17 In some of the following examples, reference is made to
18 the degree of branching in the olefin product stream
19 after passage over the isomerization catalyst.
20 Information on the degree of branching was obtained by
21 hydrogenating the olefin product mixture to paraffins
22 using a carbon-supported nickel catalyst at 210°C and
23 1000 psi of hydrogen. The mixture of linear and branched
24 paraffins was then analyzed by gas chromatography (GC)
25 using a HP Ultra-1 boiling point column. The linear
26 paraffin was assumed to have originated from linear
27 olefins and the other paraffins from branched olefins.
28 GC analysis indicated that most of the branched compounds
29 were methyl alkanes. The position of this methyl group
30 on the main chain appeared random. The percent alpha-
31 olefin present was obtained by ¹³C NMR.

32

33 Standard procedures were used to measure drilling fluid
34 properties. Kinematic viscosity was measured by ASTM
35 Method D 445-4.

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01 The standard ASTM test for pour point was found to be
02 unsatisfactory for the olefin mixtures of this invention.
03 Because of the variety of structures and carbon numbers
04 in many of these mixtures, non-uniform results were
05 obtained upon cooling. For example, some samples
06 partially solidified on cooling, but nonetheless gave low
07 pour point values as measured by the ASTM method.
08 Therefore, pour points were assessed using the following
09 procedure. A sample was placed in a bath at -10°C for at
10 least two days. Samples that froze, precipitated solids,
11 gelled, or turned turbid or hazy were judged to have pour
12 points above -10°C. For these samples, cloud points were
13 used in place of pour points. Cloud points were
14 determined using ASTM method D 2500-88. Samples that
15 could be poured and preferably were also transparent were
16 deemed to be safe for use at temperatures of -10°C.

17

18

Example 1

19

Alpha-Olefin Isomerization

20

21 A mixture containing equal weights of commercially
22 available 1-tetradecene, 1-hexadecene, and 1-octadecene
23 from Chevron Chemical Company, Houston, TX, was passed
24 over a Pt-SAPO catalyst at 180°C and a WHSV of 1.0. The
25 catalyst was prepared in a manner similar to Example 1 of
26 U.S. Patent No. 5,082,956. The product mixture contained
27 less than 5% alpha-olefin and about 24 wt % of the
28 product mixture was branched. At 100°C, the product had
29 a viscosity of 1.4 cSt, and its pour point was below
30 -10°C. The skeletal composition of the product is shown
31 in Table I.

32

33

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-15-

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Table I				
carbon #	% linear	% methyl branch	% other branch	% total branched
C14	77	20	3	23
C16	76	21	3	24
C18	75	22	3	25

Example 2Alpha-Olefin Isomerization

A mixture of commercially available alpha-olefins was prepared. It contained 35% 1-tetradecene, 30% 1-hexadecene, 27% 1-octadecene, 4% 1-eicocene, 3% 1-dococene, and 1% 1-tetracocene. The mixture was passed over the catalyst of Example 1 at 180°C and WHSV = 0.58. The product mixture contained less than 5% alpha-olefin by ^{13}C NMR, and about 35 wt % of the total product mixture was branched. At 100°C, the product had a viscosity of 1.6 cSt, and its pour point was below -10°C.

Example 3Alpha-Olefin Isomerization

The procedure of Example 1 was repeated at 200°C and a WHSV of 2.6. The product mixture contained less than 20% alpha-olefin by ^{13}C NMR analysis, and about 25 wt % of the total product mixture was branched. Data on the degree of branching are shown in Table II. At 100°C, the product had a viscosity of less than 1.7 cSt, and its pour point was below -10°C.

Table II				
carbon #	% linear	% methyl branch	% other branch	% total branched
C14	76	20	4	24
C16	74	22	4	26
C18	74	23	3	26

-16-

01

Example 4

02

Linear Internal Olefins Via Isomerization

03

04

05 Commercially available 1-hexadecene was passed over the
06 catalyst from Example 1 at 125°C and a WHSV of 0.7. The
07 product contained less than 26% 1-hexadecene by GC. The
08 remainder of the product was a mixture of substantially
09 linear internal hexadecenes containing less than 10%
10 branched olefin. The pour point of the product mixture
11 was -7°C, compared to 9°C for 1-hexadecene. The
12 kinematic viscosity at 100°C was unchanged at 1.3 cSt.

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Example 5

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Preparation and Testing of a Drilling Fluid

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17 The following Examples describe the preparation and
18 testing of drilling fluids in the laboratory. The invert
19 emulsions were prepared by mixing the other components
20 into the base fluid using a Gifford Wood homogenizer.
21 The ingredients were added in the order: viscosifier,
22 lime, emulsifier, rheological modifier (if any), brine,
23 and fluid loss additive (if any). The slurry was allowed
24 to attain a temperature of 120°F while mixing in the
25 homogenizer. The slurry was then transferred to a
26 conventional mixture and the barite added with stirring.
27 Rheological properties of the resulting drilling fluid
28 were determined at 120°F, initially, and after
29 hot-rolling at the specified temperature, typically
30 150°F.

31

32 The product of Example 2 was formulated into a 70/30
33 hydrocarbon/water ratio, 12 lb/gal drilling fluid. Two
34 compositions were prepared, with and without a fluid loss
35 additive:

-17-

01	Component	Fluid A	Fluid B
02	Product from Example 2	2250 ml	2250 ml
03	Organoclay Viscosifier	32 g	32 g
04	Lime	43 g	43 g
05	Emulsifier	86 g	86 g
06	Rheological Modifier	11 g	11 g
07	30% Calcium Chloride Brine	832 ml	832 ml
08	Barite	2894 g	2894 g
09	Fluid Loss Additive	0 g	65 g

09 The drilling fluid compositions had the following
10 rheological properties, measured at 120°F.
11

12	Parameter	Fluid A	Fluid B
13	Fann Dial Reading @ 600 rpm	62	64
14	Fann Dial Reading @ 300 rpm	41	43
15	Fann Dial Reading @ 3 rpm	6	7
16	Plastic Viscosity, cps	21	21
17	Yield Point, lb/100 sq ft	20	22
18	10 s gel strength, lb/100 sq ft	8	7
19	10 m gel strength, lb/100 sq ft	10	10

20 The drilling fluids were hot rolled at 150°F for 16 hr
21 and the rheological properties redetermined:
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-18-

Parameter	Fluid A	Fluid B
Fann Dial Reading @ 300 rpm	33	34
Fann Dial Reading @ 3 rpm	7	8
Plastic Viscosity, cps	20	22
Yield Point, lb/100 sq ft	13	12
10 s gel strength, lb/100 sq ft	10	11
10 m gel strength, lb/100 sq ft	13	17
Electrical Stability @ 120°F, V	1150	1130
PPT Test: 250°F, Grade 2 disk, 2500 psid		
Spurt Loss, ml	0.0	0.0
Filtrate Volume, ml	2.3	1.3
PPT Value, ml	4.6	2.6
Filter Cake, 32 nd	2	2
HTHP filtrate @ 300°F, 500 psi	8.6	7.5
Cake Thickness, HTHP, 32 nd	2	2
PPT Test: 350°F, Grade 2 disk, 2500 psid		
Spurt Loss, ml	1.7	1.0
Filtrate Volume, ml	5.7	2.2
PPT Value, ml	13.1	5.4
Filter Cake, 32 nd	2	2

These data demonstrate that a stable invert emulsion drilling fluid can be prepared using an isomerized olefin mixture of this invention as the continuous phase.

Additionally, the formulation (Fluid A) without any fluid loss additive had good filtration properties at 300°F and 350°F. Filtration control can easily be reduced by the addition of a fluid loss additive.

Example 6

Preparation and Testing of a Drilling Fluid

The product of Example 2 was formulated into a 70/30 oil/water ratio, 12 lb/gal drilling fluid. For comparative purposes, a drilling fluid was also prepared using a state of the art synthetic hydrocarbon, Synfluid® 2 cSt. Polyalphaolefin, available from Chevron Chemical Company, Houston, TX.

-19-

Component	Fluid C	Fluid D
Product from Example 2	2250 ml	
2 cSt PAO	0	2250 ml
Organoclay Viscosifier	54 g	54 g
Lime	65 g	65 g
Emulsifier	130 g	130 g
30% Calcium Chloride Brine	832 ml	832 ml
Barite	2895 g	2895 g
Fluid Loss Additive	151 g	151 g

The drilling fluid compositions had the following rheological properties, measured at 120°F.

Parameter	Fluid C	Fluid D
Fann Dial Reading @ 600 rpm	70	121
Fann Dial Reading @ 300 rpm	40	71
Fann Dial Reading @ 3 rpm	4	9
Plastic Viscosity, cps	30	50
Yield Point, lb/100 sq ft	10	21
10 s gel strength, lb/100 sq ft	5	9
10 m gel strength, lb/100 sq ft	7	10

The drilling fluids were hot rolled at 300°F for 12 hr and the rheological properties redetermined.

Parameter	Fluid C	Fluid D
Fann Dial Reading @ 600 rpm	72	102
Fann Dial Reading @ 300 rpm	41	58
Fann Dial Reading @ 3 rpm	5	4
Plastic Viscosity, cps	31	44
Yield Point, lb/100 sq ft	10	14
10 s gel strength, lb/100 sq ft	5	4
10 m gel strength, lb/100 sq ft	9	9
HTHP filtrate @ 400°F, 500 psi	9	8
Cake Thickness, HTHP, 32 nd	3	2
Electrical Stability @ 120°F, V	430	520

These data show that a drilling fluid formulated with the olefin mixture has better high temperature stability than a state of the art drilling fluid formulated with 2 cSt PAO. Overall, the high temperature stability of the emulsion was excellent. Additionally, Fluid C exhibited

-20-

01 a lower viscosity which would be advantageous by
02 providing a faster drilling type fluid.

03

04 Example 705 Preparation and Testing of a Drilling Fluid

06

07 A mixture of equal weights of linear internal
08 tetradecenes, hexadecenes, and octadecenes was prepared
09 by double bond isomerization of the normal alpha olefins.
10 The mixture had less than 10% branched olefin. The
11 mixture was formulated into a drilling fluid with the
12 following composition:

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20 The drilling fluid composition had the following
21 rheological properties, measured at 120°F, before and
22 after hot rolling at 150°F for 16 hrs.

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C ₁₄₋₁₈ olefin mixture	2250 ml
Organoclay Viscosifier	54 g
Lime	65 g
Emulsifier	130 g
30% Calcium Chloride Brine	832 ml
Barite	2895 g

Parameter	Initial Value	Value After Aging
Fann Dial Reading @ 600 rpm	50	59
Fann Dial Reading @ 300 rpm	28	35
Fann Dial Reading @ 3 rpm	3	5
Plastic Viscosity, cps	22	24
Yield Point, lb/100 sq ft	6	11
10 s gel strength, lb/100 sq ft	4	5
10 m gel strength, lb/100 sq ft	5	7
Electrical Stability @ 120°F, V	439	528

32 These data show that a functional drilling fluid can be
33 formulated using linear internal olefins as the synthetic
34 hydrocarbon continuous phase.

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Example 8Preparation and Testing of a Drilling Fluid

Commercially available 1-tetradecene (purchased from Chevron Chemical Co., Houston, Texas) was formulated into a drilling fluid with the following composition:

1-tetradecene	2250 ml
Organoclay Viscosifier	54 g
Lime	65 g
Emulsifier	130 g
30% Calcium Chloride Brine	832 ml
Barite	2895 g

The drilling fluid composition had the following rheological properties, measured at 120°F, before and after hot rolling at 150°F for 16 hrs.

Parameter	Initial Value	Value After Aging
Fann Dial Reading @ 600 rpm	31	34
Fann Dial Reading @ 300 rpm	16	19
Fann Dial Reading @ 3 rpm	1	1
Plastic Viscosity, cps	15	15
Yield Point, lb/100 sq ft	6	4
10 s gel strength, lb/100 sq ft	2	3
10 m gel strength, lb/100 sq ft	3	3
Electrical Stability @ 120°F, V	368	302

These data show that a functional drilling fluid can be formulated with 1-tetradecene as the synthetic hydrocarbon continuous phase.

Example 9Preparation and Testing of a Drilling Fluid

A linear internal octadecene mixture containing less than 10% branched product was formulated into a drilling fluid with the following composition:

-22-

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Linear Octadecenes	2250 ml
Organoclay Viscosifier	54 g
Lime	65 g
Emulsifier	130 g
30% Calcium Chloride Brine	832 ml
Barite	2895 g

07 The drilling fluid, composition had the following
08 rheological properties, measured at 120°F, before and
09 after hot rolling at 150°F for 16 hr.

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Parameter	Initial Value	Value After Aging
Fann Dial Reading @ 600 rpm	67	69
Fann Dial Reading @ 300 rpm	40	41
Fann Dial Reading @ 3 rpm	8	8
Plastic Viscosity, cps	27	28
Yield Point, lb/100 sq ft	13	13
10 s gel strength, lb/100 sq ft	8	8
10 m gel strength, lb/100 sq ft	11	9
Electrical Stability @ 120°F, V	739	771

Example 10

Toxicity Testing

The acute toxicity of the drilling fluids towards 4-6 day old mysid shrimp (*Mysidopsis bahia*) was determined. Statistical analysis of the test results and calculation of a 96 hr LC₅₀ were performed using procedures recommended and approved by the US EPA. The LC₅₀ is the concentration of a test sample that produces 50% mortality in the test organisms and can be used as a measure of that sample's acute toxicity. Samples having an LC₅₀ of greater than 30,000 ppm is defined as a pass, i.e., these samples have minimal toxicity.

The bioassays were conducted using the suspended particulate phase (SPP) of the drilling fluid following the United States Environmental Protection Agency protocol in Appendix 3 of "Effluent Limitation Guidelines

-23-

01 and New Source Performance Standards: Drilling Fluids
02 Toxicity Test," Federal Register Vol. 50, No. 165,
03 34631-34636. The SPP is the unfiltered supernatant
04 extracted from a stirred 1:9 mixture of the drilling
05 fluid and sea water which has been allowed to settle 1
06 hr.

07
08 Initially, a 48 hr range finder test was performed with
09 ten mysid shrimp being added to each of five
10 concentrations (3%, 10%, 25%, 50%, and 100% SPP) and a
11 sea water control, without replication. Based on the
12 results of the range-finding test, the definitive 96 hr
13 bioassay was initiated with test solutions of 3%, 10%,
14 25%, 50%, and 100% SPP for the sample. Twenty mysids
15 were added to each of the five concentrations of the test
16 solution (SPP) and to the sea water control. Three
17 replicates were used. Water quality parameters were
18 measured and observations of test animals were made at 24
19 hr intervals. After 96 hr, the test was terminated.

20

21 The drilling fluid from Example 9 had a LC_{50} of greater
22 than 1,000,000 ppm. These data demonstrate that these
23 mostly linear olefin mixtures are minimally toxic when
24 used as the continuous phase for a synthetic hydrocarbon-
25 based drilling fluid.

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01 WHAT IS CLAIMED IS:

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04 1. A fluid used in subterranean oil and gas wells
05 comprising a mostly linear olefin mixture wherein
06 the olefins have at least 12 carbon atoms.

07

08 2 A fluid used in subterranean oil and gas wells
09 comprising a mostly linear olefin mixture prepared
10 by partially isomerizing a feed containing one or
11 more linear olefins having at least 12 carbon atoms.

12

13 3. A fluid according to Claim 2 wherein said feed
14 linear olefins are alpha-olefins.

15

16 4. A fluid according to any one of Claims 1 or 2 or 3,
17 wherein the kinematic viscosity of said olefin
18 mixture is between 1 and 3 cSt when measured at
19 100°C and the pour point is below 0°C.

20

21 5. A fluid according to any one of Claims 1 or 2 or 3,
22 wherein the kinetic viscosity of said olefin mixture
23 is between 1.3 and 1.7 cSt when measured at 100°C
24 and the pour point is below -9°C.

25

26 6. A fluid according to any one of Claims 1 or 2 or 3
27 or 4 or 5, wherein said olefin mixture comprises
28 olefins having between 12 and 24 carbon atoms.

29

30 7. A fluid according to any one of Claims 1 or 2 or 3
31 or 4 or 5 or 6, further blended with a branched
32 hydrocarbon.

33

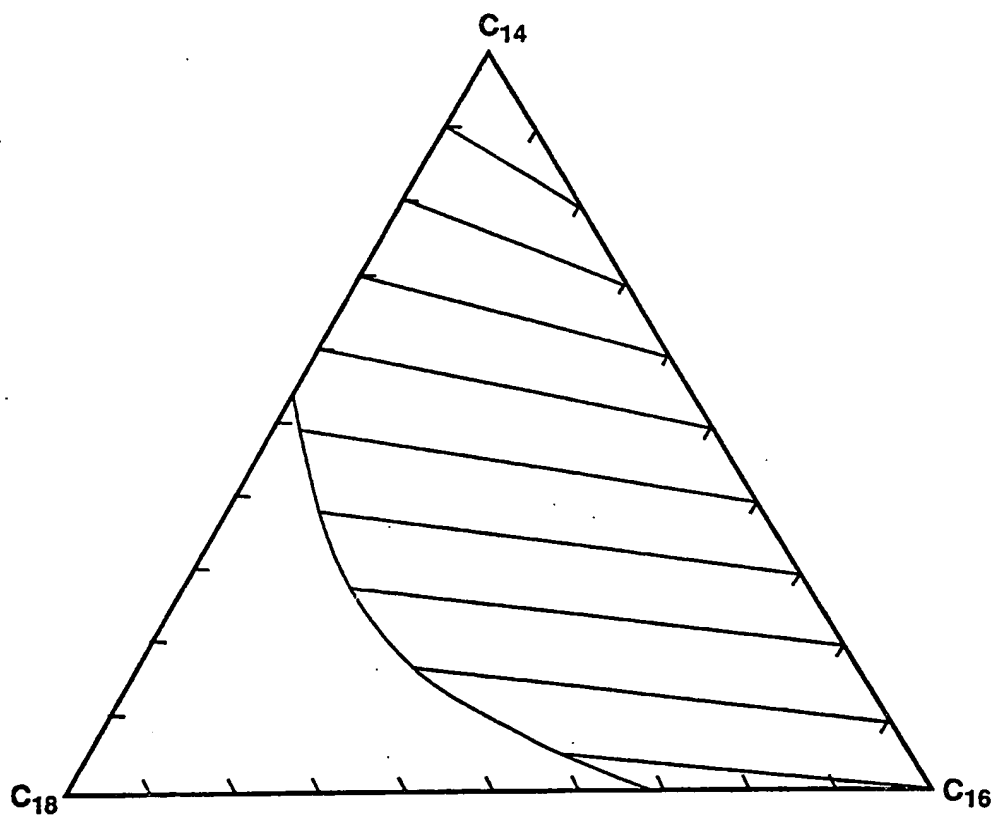
34 8. A fluid according to any one of Claims 1 or 2 or 3
35 or 4 or 5 or 6 or 7, further blended with a branched
hydrocarbon comprising a polyalphaolefin.

-25-

- 01 9. A fluid according to any one of Claims 1 or 2 or 3
02 or 4 or 5 or 6 or 7 or 8, wherein said fluid is the
03 continuous phase of a synthetic hydrocarbon-based
04 drilling fluid.
05
- 06 10. An invert emulsion drilling fluid comprising:
07
08 (a) a continuous phase, comprising a mixture of
09 mostly linear olefins with at least 12 carbon
10 atoms;
11 (b) a weight material; and
12 (c) water.
13
- 14 11. A drilling fluid according to any one of Claims 1 or
15 2 or 10, wherein said olefin mixture comprises
16 olefins having between 14 and 18 carbon atoms.
17
- 18 12. A drilling fluid according to any on of Claims 1 or
19 2 or 10, wherein the olefin mixture comprises a C₁₄
20 normal alpha-olefin.
21
- 22 13. A drilling fluid according to Claim 2 wherein said
23 feed linear olefins have between 14 and 18 carbon
24 atoms.
25
- 26 14. A drilling fluid according to Claim 10 containing up
27 to 70% water by volume.
28
- 29 15. A fluid according to any one of claims Claim 1 or 2
30 or 3 or 4 or 5 or 6 or 7 or 8 or 9 or 10 or 11 or 12
31 or 13 or 14, further comprising one or more
32 additives, at least one of which is selected from
33 the group consisting of emulsifiers, wetting agents,
34 viscosifiers, densifiers, and fluid-loss
35 preventatives.

1/1

FIGURE



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 95/01263

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C09K 7/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EDOC, WPI, USPM

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 5045219 (D.O. TRAHAN ET AL.), 3 Sept 1991 (03.09.91), claims 1,3 --	1
P,X	EP, A1, 0627481 (ALBEMARLE CORPORATION), 7 December 1994 (07.12.94), claims 1-2,4 --	1,4,6,10,11
A	US, A, 4404109 (J. TELLIER ET AL.), 13 Sept 1983 (13.09.83), claims 10-11 -- -----	1,10

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

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- * "E" earlier document but published on or after the international filing date
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- * "O" document referring to an oral disclosure, use, exhibition or other means
- * "P" document published prior to the international filing date but later than the priority date claimed

* "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

* "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search

Date of mailing of the international search report

5 April 1995

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Name and mailing address of the International Searching Authority/Authorized officer



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INTERNATIONAL SEARCH REPORT
Information on patent family members

25/02/95

International application No.

PCT/US 95/01263

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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US-A- 4404109	13/09/83	AU-B- 526600 AU-A- 5273079 BE-A- 879976 CA-A- 1128830 DE-C- 2953276 FR-A, B- 2440773 FR-A, B- 2468402 GB-A, B- 2032491 GB-A, B- 2053904 NL-T- 7920129 OA-A- 6379 WO-A- 8000921	20/01/83 22/05/80 12/05/80 03/08/82 22/05/86 06/06/80 08/05/81 08/05/80 11/02/81 30/09/80 31/08/81 15/05/80